American Mineralogist, Volume 87, pages 1215–1223, 2002

Ab initio quantum mechanical modeling of infrared vibrational frequencies of the OH group in dioctahedral phyllosilicates. Part I: Methods, results and comparison to experimental data

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ABSTRACT

The infrared (IR) spectra of small clusters of atoms ($[MM'(OH)_2]$ and $[MM'(OH)_2(H_2O)_6]$, where M, M' = Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}) mimicking the environment of the OH group in dioctahedral phyllosilicates have been modeled using ab initio quantum mechanical calculations. These modeling results are relevant to establishing the connections between IR spectra of phyllosilicates and their composition, and to investigate the utility of quantum mechanical models for calculating IR frequencies of minerals. This study focused on the OH stretch and in-plane bend fundamentals, because they give rise to a combination band near 4545 cm^{-1} (2.2 μm) that can be observed in imaging spectrometer or hyperspectral remote sensing data.

A comparison among results obtained using both ab initio [Hartree-Fock (HF) and Density Functional Theory (DFT)], and semi-empirical [PM3(tm)] methods, showed that the DFT model approaches IR frequency experimental values most closely.

IR spectra of phyllosilicates were modeled using the DFT method. The modeled frequencies were scaled using a mode-dependent linear transformation, and experimental frequencies were reproduced satisfactorily. The modeling results show that most of the variability observed in the OH in-plane bend fundamental of dioctahedral phyllosilicates can be explained by the effects of neighboring octahedral cations alone. Discrepancies between modeling and experimental results in the case of the OH stretch point to the existence of factors other than the nature of the neighboring octahedral cations, such as tetrahedral substitution, affecting this fundamental mode.